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Electrochemical comparative study on corrosion behavior of conventional and powder metallurgy titanium alloys in physiological conditions

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This article focuses on the electrochemical study of two titanium alloys employed in the manufacture of orthopedic implants – Ti-6Al-4V and Ti-6Al-7Nb – both of them obtained through powder metallurgy (PM). For comparative purposes, Ti-6Al-4V fabricated conventionally has also been investigated. Samples were immersed in a simulated body fluid (SBF) and incubated at 37 °C for different immersion time. Under these experimental conditions, we compared the influence of the processing method of alloys (PM or conventional) and their composition in the corrosion resistance. The corrosion resistance of these alloys in contact with SBF was evaluated with electrochemical impedance spectroscopy (EIS). The resulting impedance plots of all of them showed good reproducibility. For the lowest frequency tested (10 mHz) all of the samples showed high impedance modulus value approximately on the order of 10^6 Ω. This behavior is usually ascribed to a high corrosion protection performance. Although no significant differences in the evolution of the corrosion behavior for different immersion times has been found; the Ti-6Al-7Nb alloy processed by PM delivers a steady growth of corrosion resistance from day one until twelve weeks immersion. This sample showed the best performance between the two studied compositions. The resulting impedance plots show how powder metallurgy allows obtaining materials with similar or superior corrosion resistance in physiological conditions, than alloys obtained conventionally. Alloys characterization by scanning electron microscopy revealed no evidence of pitting corrosion phenomenon.

Titanium and its alloys are the preferred metallic material nowadays for biomedical applications like prosthesis for bone substitution and dental, heart and cardiovascular devices. The alloys more extensively used currently for these purposes are the α + β (Ti-6Al-4V) alloy and the α (CP Ti) pure titanium, depending on the type of prosthesis or implants, although other alloys like α + β (Ti-6Al-7Nb) are also used [1]. Titanium is considered as biomaterial owing its desirable properties, for example: low Young modulus, good fatigue resistance, high biocompatibility and excellent corrosion resistance compared with another conventional steel or cobalt alloy [2]. The great interest generated comes from the stability of the native oxide layer (TiO_2) and the corrosion resistance which protects the metal from additional oxidation in different atmospheres including the human body [2–4]. Unlike other types of materials, the corrosion of the titanium or its alloys can happen very quickly or slowly depending on the environmental conditions. If the body fluids present neutral pH, the materials exhibit extremely low rates of corrosion difficult to measure experimentally [2]. However, although this metal has been reported as bioinert, in the last decade several reports have warned that ions dissolved titanium into the human body can induce the release of potentially osteocyclic cytokines involved in implant loosening

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TABLE 1

Characteristics of the materials studied.

Material	Processing method	Dimension [mm][a]	Density [g cm^{-3}]	Relative density [%]
Ti-6Al-4V (F)	Conventional (Forging)	$10 \times 1 \pm 0.1$	4.43	99
Ti-6Al-4V (PM)	Powder metallurgy	$15.3 \times 3.9 \pm 0.1$	4.3 ± 0.1	96
Ti-6Al-7Nb (PM)	Powder metallurgy	$15.6 \times 3.7 \pm 0.1$	4.3 ± 0.1	95

[a] Units expressed in millimeter Ø per depth.

[1–5]. The Ti-6Al-7Nb alloy was developed in the biomedical sector with the aim of replace the Ti-6Al-4V alloy because of being a free vanadium alloy with better wear resistance and superior behavior in the casting processing. It is designed for hip and femur prosthesis, spine components, staples and wireless, owing its high resistance, good ductility and toughness and excellent biocompatibility due to the passive stable and dense oxide layer (Nb_2O_5) [6].

Powder metallurgy (PM) has attracted considerable interest as a technology capable of reducing processing costs of titanium components, mainly due to higher material use and fewer machining steps. Components made by PM present similar microstructures to those manufactured by conventional metallurgy but generally contain residual porosity that may worsen the mechanical properties and affect the corrosion behavior. However, this porosity could be an advantage for biomedical applications because it reduces the modulus of elasticity and improves cell adhesion. Although the corrosion behavior of conventional titanium alloys are widely studied, the work on PM alloys are more limited and almost always performed on pure Ti or Ti alloy Ti-6Al-4V [4,7,8]. The aim of this work is to study the corrosion behavior under physiological conditions of two PM alloys Ti-6Al-4V and Ti-6Al-7Nb, and compare it with the behavior of the conventional alloy Ti-6Al-4V.

Experimental

The titanium alloy study was made with three alloys different in composition or processing method as indicated in Table 1.

Samples processed by powder metallurgy (PM) were prepared by the authors at the Department of Materials Science and Engineering of the University Carlos III, based on previous works [9,10]. Both alloys were prepared by means of uniaxial pressing (600 MPa), followed by a sintering cycle as it is shown in Fig. 1. The intermediate stage at 330 °C for the Ti-6Al-7Nb alloy is introduced to remove the wax used in the powder preparation. This

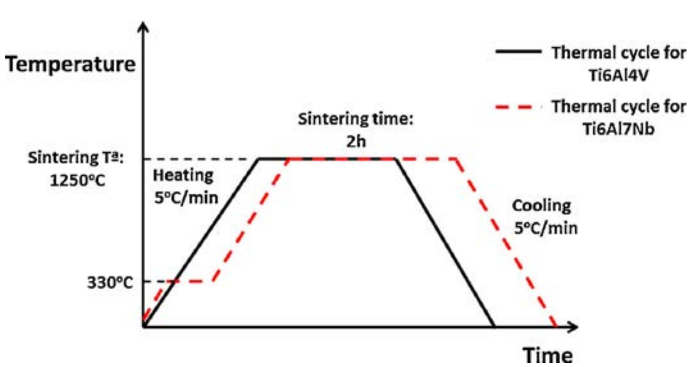

FIGURE 1

Sintering cycles for the powder metallurgy titanium alloys.

alloy was made from Ti powder and a Al:Nb master alloy. For the preparation of the Ti-6Al-4V samples, was employed prealloyed powder without lubricant addition.

Density of the sintered samples was measure geometrically to know the total porosity of the material; showing values of 96.2% for the Ti-6Al-4V alloy and 94.9% of the theoretical in the case of the Ti-6Al-7Nb (Table 1). The surfaces of all samples tested, both conventional and PM, were prepared metallographically: wet-grounding with 180–1000 microns grit silicon carbide (SiC) paper, followed by polishing with 9, 1 and 0.3 microns alumina suspensions and final polishing with a silica gel colloidal suspension to get mirror polished surfaces. After, the samples were washed with distilled water, cleaned with ethanol in an ultrasonic bath to remove any particles that may have fallen into the pores and dried by hot air. As a control, the Ti-6Al-4V ELI medical grade (Surgival SL) alloy was used.

Electrochemical impedance spectroscopic (EIS) studies

Corrosion behavior of conventional and powder metallurgy alloys were evaluated trough electrochemical impedance spectroscopy (EIS) tests after being immersed in simulated body fluid whose composition was: DMEM (Dulbecco's modified Eagle's medium), fetal bovine serum (15%) and antibiotics. All experiments were carried out with incubator, 37 °C, at 1, 7, 14, 21 days, 6 and 12 weeks as immersion time.

Impedance measurements were carried out using an Autolab Potentiostat PGSTAT302N and the impedance spectra were acquired in the frequency range from 10 mHz to 10 kHz by applying input sinusoidal signals of ±10 mV. A three-electrode electrochemical cell was used which included a platinum wire as counter electrode, an Ag/AgCl (KCl 3 M) as reference electrode and the titanium alloy sample under study as working electrode. The tested area of the surface of the working electrode was 0.28 cm^2.

Electrode potentials at open circuit were registered versus the Ag/AgCl (KCl 3 M) reference electrode whose relative potential to the standard hydrogen electrode (SHE) exhibits a value of 205 mV. Impedance data obtained were analyzed with the Zview software and fitted to different equivalent circuits which were chosen for this study. In order to verify the reproducibility of the measurements, three repetitions of all of tests were realized.

Sample surface morphology was studied by Scanning Electron Microscopy, SEM, after each immersion time (1, 7, 14, 21 days, 6 and 12 weeks).

Cell viability study

Human mesenchymal stem cells isolated from bone marrow (MSC) commercially available (Lonza) were used. Cells were seeded on the material described in Table 1 and incubated for 1, 7, 14 and 18 days. AlamarBlue reagent supplied by Biosource was employed for the cell viability quantification. This reagent

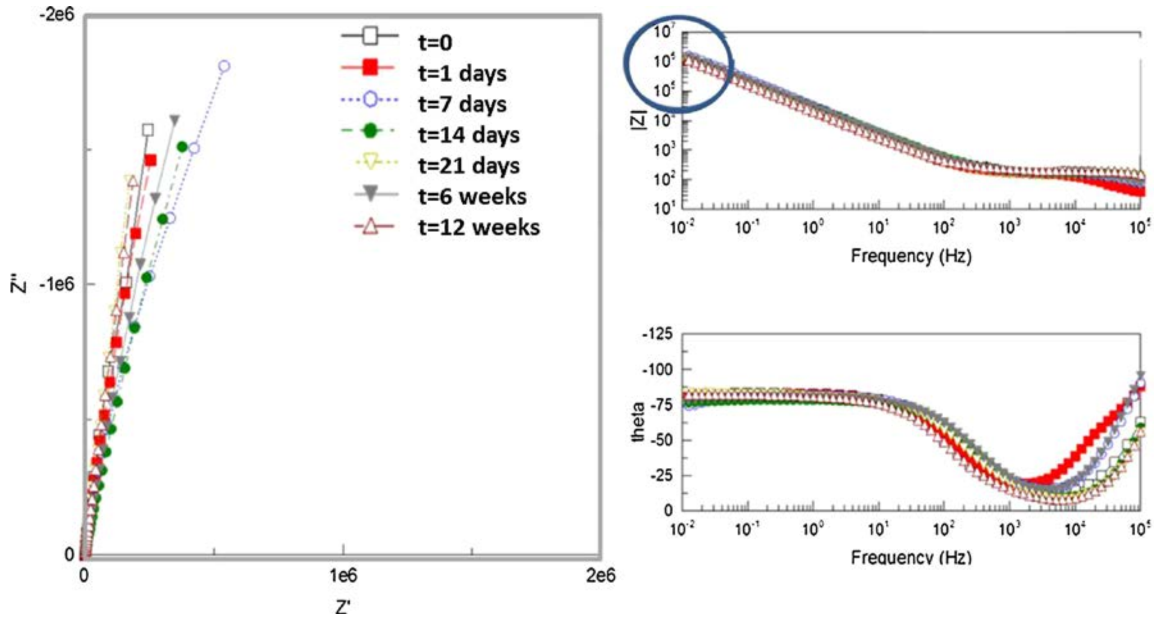

FIGURE 2

Nyquist and Bode diagrams for Ti6Al4V (F) along the immersion time from zero until twelve weeks.

contains a redox indicator which changes its color in response to the metabolic activity of the cell. Cells were washed with PBS and incubated with 10% alamarBlue fluid. After three hours incubation, the fluid was collected and, after exciting the sample at 530 nm, the fluorescence emitted at 590 nm in a spectrofluorometer Synergy4 was quantified.

Results and discussion

Figure 2 shows the impedance data for Ti-6Al-4V (F) alloys at different immersion time (0, 1, 7, 14, 21 days, 6 and 12 weeks) in simulated based fluid (SBF) represented as Nyquist and Bode plots. Figure 3 shows a more detailed view of lowest frequencies region of the Bode plots for Ti-6Al-4V (F), Ti-6Al-4V (PM) and Ti-6Al-7Nb (PM) alloys in an attempt of standing out differences in impedance behavior of each one of the samples tested. It would be difficult to observe differences in the evolution of the impedance plots in the middle and high frequencies regions of these samples. As it can be seen, all of them show a value of $|z|$ around $10^6\ \Omega$ which points out the corrosion phenomenon is hardly taken place. No significant change in their behavior was observed after 12 weeks. Some authors [4] found similar behavior after 24 hours of immersion in Ringer's solution. They associate these results with a possible spontaneous growth of fresh oxide layers that are covering the entire metal substrate.

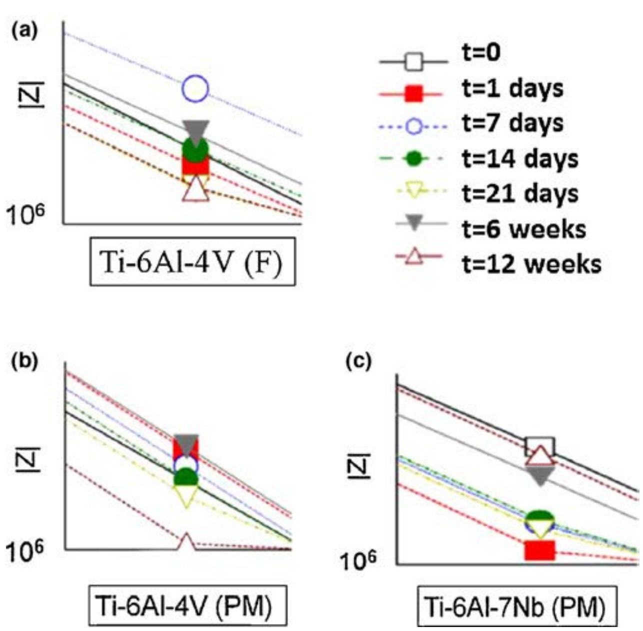

FIGURE 3

Detailed view of the impedance modulus in the Bode diagrams for the alloys: (a) Ti6Al4V (F), (b) Ti6Al4V (PM) and (c) Ti6Al7Nb (PM); for an immersion time of zero until twelve weeks.

However, slight differences can be observed from Fig. 3 such as Ti-6Al-4V (F) alloy presents its maximum impedance value for an immersion time of 14 days; decreasing these values for longer immersion time. Ti-6Al-4V (PM) alloy exhibits its maximum value for immersion tests of times one day and six weeks of duration, decreasing for the longest time of 12 weeks. The highest value for the Ti-6Al-7Nb (PM) alloy is found for the shortest but also for the longest time, 12 weeks.

High impedance values obtained from middle and low frequencies in all samples indicates that a passive oxide film grows when the metal surfaces are placed in contact with the simulated body fluid [11].

Comparison of the corrosion resistance between one day and twelve weeks immersion times

Corrosion resistance for 1 day immersion for the three alloys studied is compared in Fig. 4. Nyquist and Bode plots show almost the same behavior for the three alloys. However, as it can be seen in Fig. 5a, for an immersion time of 1 day the Ti-6Al-4V (F) alloy shows the highest impedance modulus while for twelve weeks, the powder metallurgy Ti-6Al-7Nb alloy is showing the highest value (Fig. 5b). Several previous works, have reported results on the high corrosion protection performance of the Ti-6Al-7Nb alloy due to the development of an enhanced passive film because of the

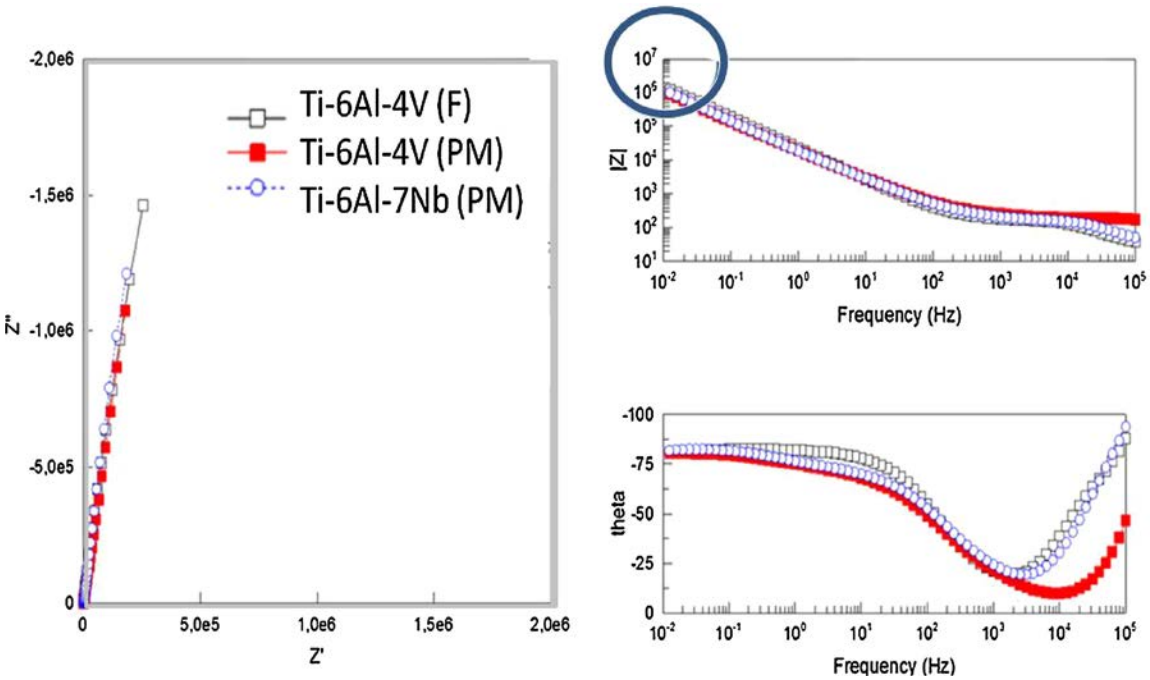

FIGURE 4

Nyquist and Bode plots for Ti6Al4V (F), Ti6Al4V (PM) and Ti6Al7Nb (PM) alloys for an immersion time of one day.

presence of the Nb in the alloy [11]. The results of this paper are in a good agreement with those studies; indicating moreover that the Ti-6Al-7Nb processed by powder metallurgy technique also shows better corrosion behavior compared to that of Ti-6Al-4V.

Choice of the equivalent circuit

González and J.C. Mirza-Rosca have obtained a good interpretation of impedance results in studies related with the corrosion behavior of titanium and some of its alloys by using two different equivalent circuits [12]. One of them is a single equivalent circuit useful for studying compact oxide films growing on the metal surface in contact with the electrolyte solution (Fig. 6a). This circuit contains several electrical elements, R_s which is associated to the aqueous solution resistance between the reference electrode and the passive film, R_p is the resistance of the passive film and C_p is capacitance of such a passive film. For studying porous passive layers these authors used a second equivalent circuit (Fig. 6b). Such a circuit was built with two electrical meshes. One of them is correlated with the electrochemical double-layer capacitance (C_{dl}) and the resistance for the charge-transfer of the corrosion process (R_{ct}), both in the base of the pores. In the second electrical mesh, R_p is associated with the ionic resistance of the pores of the passive film impregnated with electrolyte and C_p is the capacitance of the intact areas (pore-free zones) of the passive film. R_s is again associated with the aqueous solution resistance between the reference electrode and the passive film.

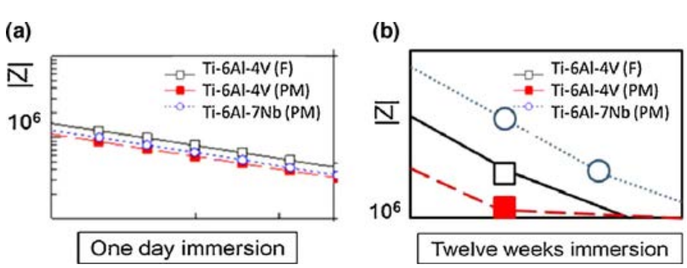

FIGURE 5

Detailed view of Bode diagrams for Ti6Al4V (F), Ti6Al4V (PM) and Ti6Al7Nb (PM) alloys for an immersion time of: (a) one day and (b) twelve weeks.

The fits obtained by the proposed equivalent electrical circuit reveal the high corrosion resistance of all the studied alloys from short to long immersion time.

Figure 7 shows Nyquist and Bode plots obtained for the Ti6Al7Nb (PM) alloy after 12 weeks of immersion in SBF and the plots obtained from the fit results by applying the equivalent circuit in Fig. 6b. Instead of the C_p and C_{dl} capacitances showed in Fig. 6b, two constant phase elements CPE (which represent the deviation from an ideal capacitive behavior) were used. The impedance of a CPE is given by [12]:

$$Z_{CPE} = \frac{1}{Q\dot{c}(j\omega)^{\alpha}} \tag{1}$$

where $j = \sqrt{-1}$, ω is the angular frequency in rad/s, $\omega = 2\pi f$, and f is the frequency in Hz. The CPE is defined by two parameters Q and α, where Q has units of s^{α}/Ω or $Fs^{\alpha-1}$ and α is a dimensionless number. α is related to a non-uniform current distribution due to the surface roughness or other distributed properties, and varies between 0 and 1. The CPE reduces to a Warburg element representing semi-infinite length diffusion phenomena for $\alpha = 0.5$ and to an ideal capacitor for $\alpha = 1$.

SEM analyses were performed on the samples surfaces to characterize possible changes after each immersion time. Figure 7 shows the micrographs obtained for all alloys, Ti-6Al-4V (F), Ti-6Al-4V (PM) and Ti-6Al-7Nb (PM), after 21 days immersion. It was chosen this immersion time to exemplify because there were no significant morphological changes along the various immersion times tested. No pitting, cracks, or other defects appeared on the

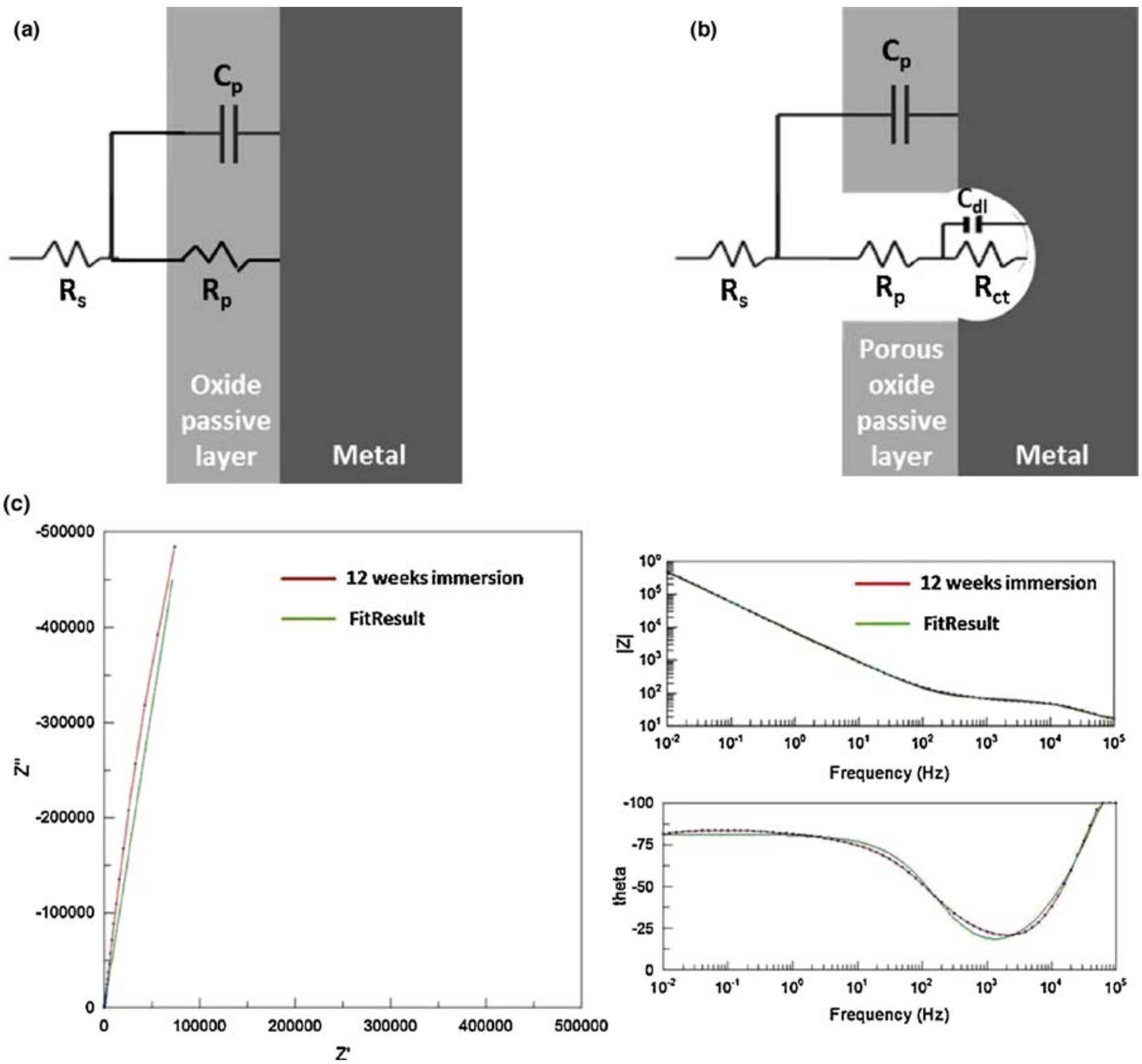

FIGURE 6

Equivalent electrical circuit for the analysis of the impedance spectra for: (a) a compact oxide passive layer with R_s, R_p and C_p elements and (b) a porous oxide passive layer with R_s, R_p, C_p, R_{ct} and C_{dl} elements; and (c) Nyquist and Bode plots with the fit results obtained by the application of (b) for the Ti6Al7Nb (PM) alloy after 12 weeks of immersion in SBF.

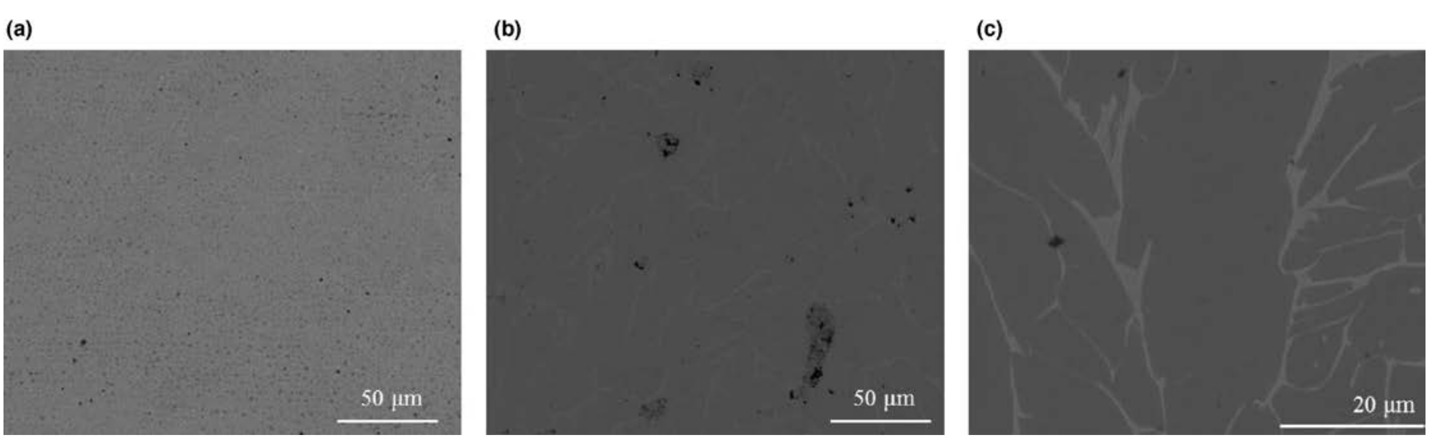

FIGURE 7

SEM micrographs of the alloys for a twenty-one day immersion: (a) Ti6Al4V (F), (b) Ti6Al4V (PM) and (c) Ti6Al7Nb (PM).

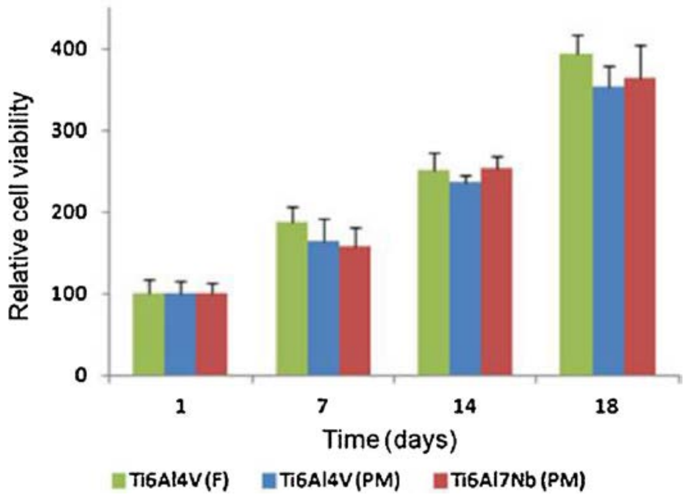

FIGURE 8

MSC cell viability grown on Ti6Al4V (F), Ti6Al4V (PM) and Ti6Al7Nb (PM).

metal surfaces in the presence of the simulated body fluid in physiological conditions. These results are in a good agreement with the impedance spectroscopic studies.

Cell viability study

Figure 8 presents the MSC viability of cells grown on Ti-6Al-4V (F), Ti-6Al-4V (PM) and Ti-6Al-7Nb (PM) alloys. As it can be seen, the viability of that grown cells increased with the immersion time (from 1 to 18 days) for the powder metallurgy alloys similarly to the conventional Ti-6Al-4V alloy. MSC cells were adhered to the three test surfaces regardless of their composition or the processing technique used. Other research works [13,14] have been conducted in similar conditions of cell cultures using Dulbecco's modified essential medium (DMEM) and Human mesenchymal stem cells (MSCs) in order to obtain and compare the cell behavior in different surfaces tested.

Conclusions

(1) The three studied alloys: Ti-6Al-4V (F), Ti-6Al-4V (PM) and Ti-6Al-7Nb (PM) show excellent corrosion resistance ($|z| > 10^6\ \Omega$) in physiological conditions from day one until twelve weeks immersion.
(2) Fits obtained by the chosen equivalent electrical circuit reveal the high corrosion resistance of all the studied alloys from short to long immersion time.
(3) Although no significant differences in the evolution of the corrosion behavior, for different immersion times it has been found; the Ti-6Al-7Nb alloy processed by PM delivers a steady growth of corrosion resistance from day one until twelve weeks immersion; showing the best behavior between the three alloys.
(4) It has been shown how powder metallurgy allows obtaining materials with similar or superior corrosion resistance in physiological conditions than alloys obtained conventionally.
(5) MSC viability of cells grown on Ti-6Al-4V (PM) and Ti-6Al-7Nb (PM) alloys is similar to the conventional Ti-6Al-4V alloy.

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